

Photoelectron diffraction at the surface of amorphous carbon nitride

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The line shape of N 1s photoemission spectra in a certain type of amorphous carbon nitride is shown to depend strongly on the polar angle of photoelectron emission. This effect is explained in terms of photoelectron forward scattering due to preferential orientation of bonds near the surface. An alternative model based on different indepth distributions for each of the nitrogen chemical species does not provide a satisfactory explanation of the observed angular dependence. The changes with polar emission angle of the photoelectron and Auger electron spectra are compared to elucidate the nature of each of the N 1s photoemission peaks. © 2000 American Institute of Physics. [S0003-6951(00)02947-8]

There is currently a large research effort on amorphous carbon nitride ($a\text{-CN}_x$) motivated by its outstanding mechanical and tribological properties.^{1,2} The understanding of the local structure of $a\text{-CN}_x$ is essential for optimizing its properties, but the atomic structure of this material is not well known. This is mainly due to the rich variety of local environments and the lack of long range order. Various diffraction techniques have been used so far, such as neutron diffraction,³ electron diffraction,⁴ and x-ray diffraction,⁵ but only averaged radial distributions of neighbors have been obtained and little insight about the nature of local structure has been gained. Fullerene-like and graphite-like structures have been found in annealed $a\text{-CN}_x$ with transmission electron microscopy,¹ but the role of nitrogen in these structures is not fully understood.

X-ray photoemission spectroscopy has also been widely used to study amorphous carbon nitride, but the interpretation of the spectra is still matter of discussion.^{1,6–10} Marton and co-workers⁸ proposed that the two main peaks in the N 1s spectra (at 400.9 and 398.4 eV) correspond to nitrogen bonded to sp^2 and sp^3 carbon, respectively. But an experimental study of the PEXAFS effect (photoemission extended x-ray absorption fine structure) in the N 1s photoemission spectra, showed that the peak 398.4 is most likely due to double and triple bonds, and not to sp^3 hybridization.¹¹ This PEXAFS experiment was done on $a\text{-CN}_x$ samples showing negligible photoemission angle dependence to avoid photo-

electron diffraction effects. In this letter, we present further evidence that we hope will elucidate the interpretation of the N 1s peak at 398.4 eV.

The samples were prepared *in situ* by low energy (80 ± 20 eV) nitrogen ion bombardment of amorphous carbon at 800 °C. The high substrate temperatures and low ion energies used during nitrogen implantation have led to a structure with preferential orientation of bonds near the surface, and this has made possible the observation of photoelectron diffraction effects that are not detectable in $a\text{-CN}_x$ samples prepared with conventional preparation conditions.¹¹

The electron spectra were measured with a VG Escalab 210 spectrometer, using Mg $K\alpha$ radiation (1253.6 eV), 7° analyzer acceptance semi-angle, and 0.9 eV energy resolution. Rotation of the sample allowed the emission polar angle θ to be varied from 0° to 80° relative to the surface normal axis. The radiation source and the electron analyzer were kept fixed, the angle between them being 60°.

Figure 1 shows N 1s photoemission spectra at two representative electron emission angles. In the following, we will refer to the two main N 1s peaks as peak 1 (400.9 eV), and peak 2 (398.4 eV). A third intermediate peak at 399.3 eV is observed under certain conditions,¹⁰ but seems to be quite weak in the present case, as good quality fits to the spectra can be obtained with Gaussian line shapes without considering this intermediate peak.

Peak 2 drastically diminishes its intensity as the sample is rotated slightly off the normal emission direction. Two possible reasons for this behavior are (i) different indepth distributions of different N species (buried layer model) and (ii) photoelectron diffraction. Most likely, the observed angular dependence is due to a convolution of both effects, but

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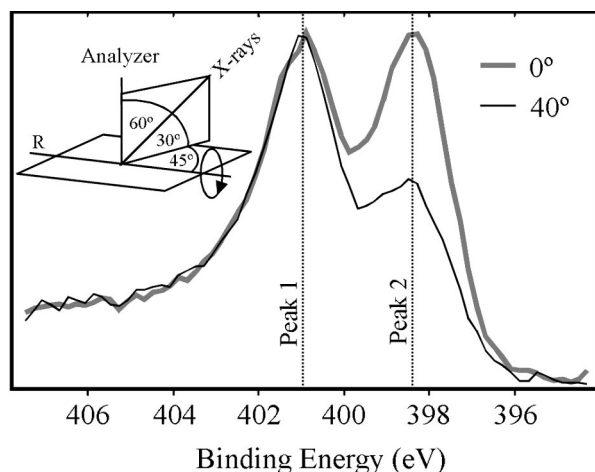


FIG. 1. N 1s photoemission spectra at two representative emission polar angles. Polar angle is defined as zero when the sample surface normal axis is parallel to the analyzer axis. Experimental geometry at zero polar angle is shown in the upper left corner of the figure. Letter R corresponds to the polar rotation axis.

from the analysis that follows, one can conclude that photoelectron diffraction is a major effect, whereas the buried layer model cannot explain alone the observed angular distributions.

(i) In the buried layer model the variation of the photoemission intensity as a function of polar angle $I(\theta)$ is determined by the depth profile $n(z)$ as

$$I(\theta) = \frac{I_0}{\lambda} \int_0^\infty n(z) e^{-z/\lambda \cos \theta} dz, \quad (1)$$

where n is the concentration of the corresponding chemical species as a function of depth z , λ is the attenuation length (15 Å in the present case¹²), and θ is the electron emission angle. Assuming that all nitrogen atoms contributing to peak 2 are in the bulk, the latter would have maximum intensity for normal emission, because in this condition the length of the photoelectron path inside the solid is minimum. The outermost layer thickness has been used as an adjustable parameter to fit the calculations to the experimental data. Figure 2 shows the experimental result at 398.4 eV binding energy (solid circles) along with the best fit for the buried layer model (thick dashed curve). In Fig. 2, the experimental data at 400.9 eV is also shown for comparison and seems to be almost flat. The weak oscillations of the peak at 400.9 eV could be due to a number of factors: inelastic loss processes, experimental errors, or photoelectron diffraction effects.

The fitted thickness D of the overlayer is 4.2λ (approximately 60 Å). The other free parameter in our model, the concentration of type 2 nitrogen atoms in the bulk, attained in the fitting procedure its maximum possible value, that corresponding to a 100% nitrogen substrate. A lower value for this parameter results in a lower quality fit to the experimental data. Therefore, the buried layer model leads to an unrealistic depth profile and a poor quality fit to the experimental data.

(ii) Although the sample is amorphous as determined by *in situ* reflection high energy electron diffraction, preferential orientation of atomic bonds at the surface cannot be ruled out. We have calculated the angular dependence of N 1s

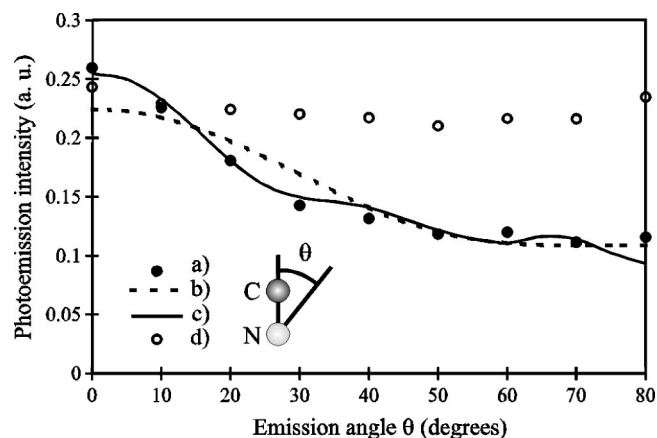


FIG. 2. Comparison of various theoretical models with the experimental data on the angle dependence of the N 1s photoemission peak 2 (398.4 eV). (a) Experimental data at 398.4 eV binding energy. (b) Buried layer model for the data at 398.4 eV. (c) N 1s photoelectron diffraction model for the data at 398.4 eV (including instrumental broadening and orientational disorder). (d) Experimental data at 400.9 eV binding energy. Peak intensities are relative to the intensity of the background at 394 eV binding energy. Experimental intensities were taken from a single point (at either 398.4 or 400.9 eV) in the photoemission spectra. The scheme in the lower part shows the geometry used in the electron multiple scattering calculations. Emitter is the nitrogen atom.

photoelectrons scattered by a carbon atom located on top of the emitter at a distance corresponding to a CN triple bond, using a curved wave multiple scattering approach.¹³ The results of this calculation are compared with the experiment and the buried layer model in Fig. 2 (thin solid curve). In order to account for both the finite instrumental angular resolution ($\pm 7^\circ$) and some degree of orientational disorder, the calculated photoelectron diffraction intensity has been convoluted with a Gaussian broadening profile. The width of the Gaussian has been used as an adjustable parameter to fit the experimental data and a value of $\pm 7.6^\circ$ has been obtained, in good agreement with the instrumental broadening. The contribution to peak 2 coming from other randomly oriented CN bonds has been incorporated as an angle-independent term. From this analysis, we have obtained that 21% percent of the CN bonds contributing to peak 2 are randomly oriented while 79% are oriented perpendicularly to the surface. We have also attempted to fit the experimental data with a convolution of the buried layer model and the photoelectron diffraction model, but such a fit has too many free parameters for the solution to be uniquely determined.

We have calculated the scattering of N KVV Auger electrons (not shown in Fig. 2 for the sake of clarity) and the result is quite similar to the curve corresponding to N 1s photoemission. Therefore, one could expect some correlation between the changes in Auger and photoelectron spectra as a function of polar angle. The KVV Auger peak of N is shown in Fig. 3 at normal (0°) and grazing (80°) electron emission angles. The peak at 382 eV is due to N K $\pi\pi$ transitions. The intensity of this feature relative to the total Auger intensity is related to the density of π bonds.¹⁴ When turning the polar angle to normal emission, the N K $\pi\pi$ Auger peak grows as photoemission peak 2 grows. This suggests that peak 2 corresponds to a bonding configuration with more π bonds than that corresponding to peak 1. So far, this peak has been assigned to C–N single bonds,⁸ whereas the evidence pre-

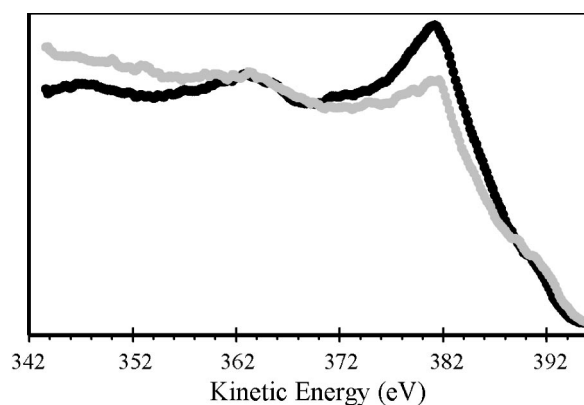


FIG. 3. KVV Auger electron spectra of N at normal (0°) and grazing (80°) emission (black and gray dots respectively).

sented here seems to indicate that this peak is due to π bonding (triple and/or double bonds).

Summarizing, we have found a strong polar emission angle dependence for both the N $1s$ photoemission and N KVV Auger spectra of a certain type of amorphous carbon nitride. We have found that a buried layer model based alone on inelastic scattering of the electrons cannot explain the observations. On the other hand, the photoelectron diffraction calculations including instrumental broadening and orientational disorder are in good agreement with the experimental data. We have correlated the changes in the N $1s$ photoemission and N KVV Auger spectra as function of polar angle and found that the N $1s$ peak at 398.4 eV is associated to strong π bonding.

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